

The University of Chicago

A METHOD FOR OBTAINING POWDERS OF UNIFORM
SODIUM CHLORIDE CRYSTALS IN VARIOUS SIZE
RANGES, AND THE EFFECT OF SIZE UPON
THE INTENSITY OF X-RAY REFLECTION

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF PHYSICS

1940

By

FITZ-HUGH MARSHALL

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A Method for Obtaining Powders of Uniform Sodium Chloride Crystals in Various Size Ranges, and the Effect of Size upon the Intensity of X-Ray Reflection

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(Received August 1, 1940)

I. A technique is presented for precipitating powders of sodium chloride crystals, uniform in size and cubical in shape, in various size ranges from 1 to 70 microns, above which the range could be extended by screening. The crystals are prepared by precipitation with absolute ethyl alcohol from a saturated solution of sodium chloride in water, but varying excess quantities of water are added to either of the solutions before combining them. Control of size range, and of crystal uniformity within a size range, is accomplished by careful attention to certain primary variables in the precipitation process, each of which produces marked changes in the character of the powder obtained. These are discussed, and a simplified procedure is presented for producing any desired size. II. This technique was developed to make possible a study of the variation of intensity of x-ray lines reflected from such size-graded powders. The 200-reflection of $\text{Cu } K\alpha$ radiation has been investigated, and a curve is shown for the variation of intensity with crystal size. The intensity decreases slightly with increase of crystal size, according to a curve which indicates that the crystals are imperfect but are more perfect than large single crystals.

I. A METHOD FOR OBTAINING POWDERS OF UNIFORM SODIUM CHLORIDE CRYSTALS IN VARIOUS SIZE RANGES

Introduction

FINE crystalline powders, rather than single large crystals, have been used in many quantitative measurements on the intensity of x-ray reflections. Comparison of results with theory has invariably involved the assumption that the individual crystals are so small, 10^{-5} cm or less, as to offer negligible x-ray absorption. Most investigators have been greatly concerned with the degree of subdivision of their powders, and a few have ground powders successively finer

until intensity determinations leveled off to constant values;¹ but on the whole, there has been no attempt at a systematic study of reflection from powders of crystals larger than allowed by simple theory. It seemed desirable, therefore, to develop a reproducible technique for making uniform crystals of various sizes and to investigate their x-ray reflections. Sodium chloride was selected for study.

Sodium chloride powders have generally been prepared either by prolonged grinding or by precipitation. Grinding produces such an irregular debris of all sizes and shapes of particles

¹ R. J. Havighurst, Phys. Rev. 28, 882, (1926).

that no precise assignment of particle size can be made, while precipitation results in comparatively uniform crystals. This paper describes the controls and variables involved in the method of precipitation with absolute ethyl alcohol from saturated sodium chloride solution in water, with varying excesses of water added to either of the solutions before combining them.

Variables controlling the precipitation process

In the present study it was found that control of size range, and of crystal uniformity within a size range, may be accomplished by careful attention to six primary variables discussed below, each of which produces marked changes in the character of the powder obtained. Since there are more variables than necessary, the problem is to find conditions under which all except one or two level off in their effects and offer no critical source of inconsistency in results.

(1) *Relative proportions of alcohol and salt solution.*—As would be expected, the size of crystals decreases with increase of the proportion of alcohol used, due to increased speed of precipitation. For obtaining the smallest crystals, proportions as high as 100 parts of alcohol to 1 part of salt solution were used. But for all other sizes, it was convenient to use approximately equal quantities of alcohol and salt solution.

(2) *Excess of water added to the salt solution.*—As increasing excesses of water are added to the originally saturated solutions of sodium chloride in water, the speed of precipitation by alcohol is decreased and larger particles are formed, as illustrated in Fig. 1B. This variable is not critical enough for use as a major control, except in limited regions. On the other hand, this uncritical nature makes it possible to eliminate a frequent source of irregularity. The addition of 5 to 10 percent of water to the saturated salt solution, which introduces no great change in size range, prevents supersaturation or pre-precipitation due to evaporation of the salt solution before combining with the alcohol. This is of special importance at high temperatures, where evaporation is rapid, and at low temperatures, where decreasing solubility leads to supersaturation.

(3) *Excess of water added to the alcohol.*—In sharp contrast to the previous case, Fig. 1A

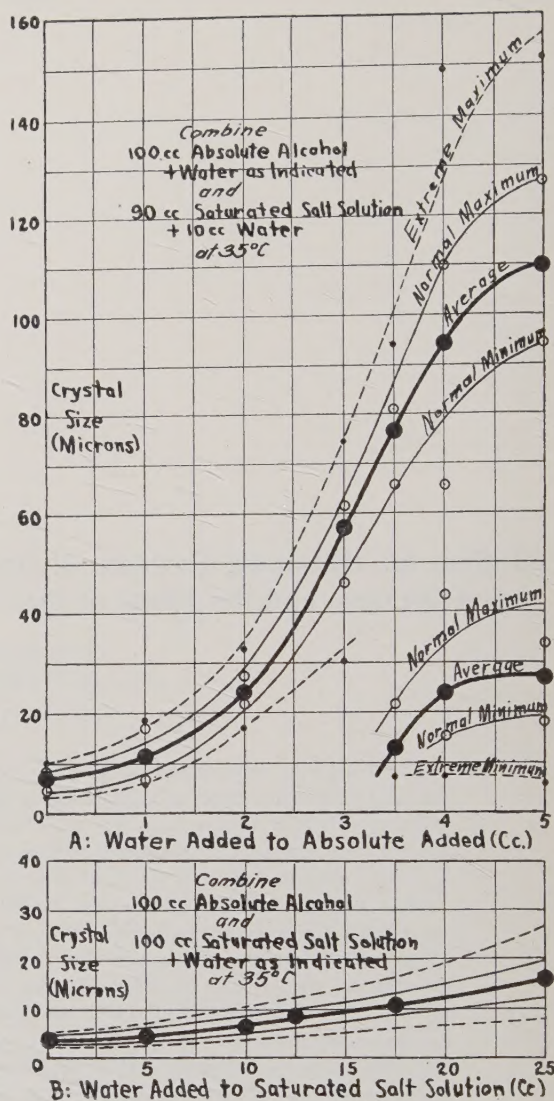


FIG. 1. Characteristic precipitation curves.

shows that as increasing quantities of water are added to commercial absolute alcohol (about 99.5 percent by volume), the size of the crystals precipitated increases rapidly. Note that the abscissa scales of Fig. 1A and 1B are different: the addition of 3 cc of water to 100 cc of salt solution causes a negligible change in the particle size, while the addition of the same 3 cc of water to the absolute alcohol multiplies the particle size by a factor of six!

As the dilution of the alcohol is extended beyond 3 percent, subsizes appear, mixed with the main large size—one subsize at first, probably several later on, although it is very difficult to

discriminate between size ranges as the curves advance. As the other variables are manipulated in this multiple region, the several mixed ranges change greatly in their average size and proportion, and occasionally they seem to converge toward a common intermediate range. But in no case has a successful precipitation been performed in which one single size resulted, uncluttered by another size range. Thus it is essential to the formation of uniform crystals that only 97 percent or higher concentration alcohol be used.

(4) *Temperature*.—In general, the higher the temperature of the solutions used in precipitation, the larger the crystals produced. Under some conditions, temperature seems to be a critical variable; but under the conditions recommended for the other five variables, temperature can be used to control particle size only by a factor of about five. However, for exact reproducibility of results and, in particular, for the maximum degree of uniformity of crystals, it appears to be essential that the alcohol and salt solution be at the same temperature when combined, and that there be no large variation of temperature during the precipitation process. For this reason, precipitations from test-tube quantities of solutions rarely are as satisfactory as from larger quantities. The thick walls of milk bottles have been found to provide a desirable degree of insulation from rapid temperature changes, making temperature control after combination unnecessary.

Temperatures ranging from the boiling point of alcohol to well below freezing were used. For small crystals, temperatures approaching the eutectic point of the salt solution were used. The smallest crystals were produced by the unusual procedure of dry-ice freezing the salt solution to a solid, then melting it in absolute alcohol.

(5) *Thoroughness of shaking during precipitation*.—Size and uniformity of powders can be greatly influenced by the degree of agitation of the combined solutions during the precipitation process. This would seem to be partly a matter of originally mixing the two solutions uniformly, partly a matter of maintaining uniform mixing on a microscopic scale while the growth of crystals continues. Little or no agitation causes

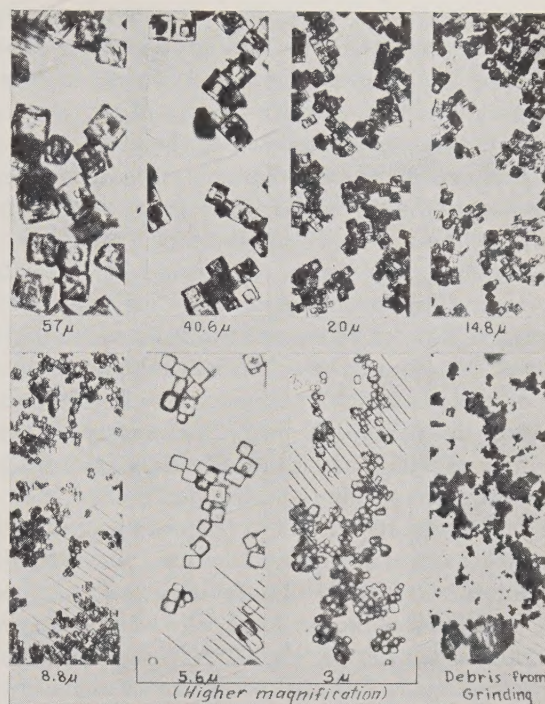


FIG. 2. Photomicrographs of crystals.

non-uniformity, with the formation of larger crystals mixed with assorted smaller sizes. Results were most consistent and reproducible when the combined solutions were shaken vigorously throughout the precipitation, and this routine was finally adopted for all cases.

(6) *Time*.—Crystal sizes are highly dependent on the elapsed time between combining the two solutions and stopping the precipitation process by vacuum filtration. Since the time required for completion of growth varies from five seconds to about four minutes, five minutes from the time of mixing to pouring into the vacuum filter assured that growth would be checked only at an advanced stage. Fast vacuum filtration (aspirator) assured a minimum of "undecided" time during which no further shaking was possible.

Miscellaneous experimental details

Commercial filter papers failed to stop the smallest crystals produced. Various other types of filters were tried—Jena fused-glass filters, porous porcelain filters, etc. Some of these stopped the particles, either immediately or after the larger openings were clogged by crystals, but

the rate of flow was too slow. It was found that filter papers cut from ordinary typewriter bond stopped the small particles and filtered rapidly!

For measuring the size of crystal particles, a fifty-division scale was used in the eyepiece of a microscope (without micrometer attachment). The sample was passed back and forth in the field of vision until the smallest particle was ascertained. The linear dimension of this was measured and recorded as the "extreme minimum." The "extreme maximum" was similarly found, followed by the "normal minimum" and "normal maximum" crystals, roughly the extremes in any typical field. This preview of the sample aided in the final selection of a single crystal representing an "average."

The reproducibility of averages thus obtained, without size distribution analysis, was usually 3 percent or better. The uniformity of size can be judged from the curves of Fig. 1 and from the photomicrographs of Fig. 2. A sample prepared by grinding is included for contrast; measured sizes vary by more than one thousand to one.

For x-ray purposes, it was necessary to pack the powders into briquets in small brass frames. In the past this has usually been accomplished by mechanical compression, as with a vise. Since such a method fractures the crystals, it could not be used for the present experiment. This difficulty was avoided by allowing the powder to settle directly into the frame during filtration and pressing gently to compact. After desiccation, the excess powder was shaved off flush with the frame with a razor blade. The last few strokes were taken as lightly as possible, and microscopic examination showed no cutting or scratching of individual crystals.

Uniform powders of very large crystals, above 30 microns, fail to adhere under the conditions just described, although smaller particles form almost marble-hard masses. But these larger particles can be made to stick together by rinsing them in the filter with salt-saturated 90 percent alcohol. Evidently a droplet of this liquid is left at each point of contact between crystals and on drying deposits enough salt to bind them. The salt-saturation of the alcohol rinse is very important: 90 percent alcohol without salt saturation noticeably dissolves and disfigures the crystals; even 70 percent alcohol,

when salt saturated, leaves no microscopic evidence of imperfection in the crystals. There may be some x-ray evidence that this process disturbs the crystalline surface.

The question has frequently arisen as to whether sodium chloride crystals continue to grow when suspended in absolute alcohol, the larger crystals at the expense of the smaller ones. When fresh absolute alcohol is used, there is no microscopically detectable growth of crystals, 3 microns or larger, even over time intervals of twelve hours or more. The increase in the settling rate of much smaller crystals is evidence that they do grow. A slight amount of water in the alcohol causes measurable growth of all sizes. For this reason, the smallest crystals, involving long filtration time, must be precipitated with such large excesses of alcohol that the water in the salt solution lowers the absoluteness of the alcohol by only negligible amounts. Growth is less rapid in cold solutions.

Simplified procedure for obtaining various size ranges

(1) For the smallest crystals, 1 to 5 microns, a 25-cc portion of saturated salt solution, with 5 percent of water added, is frozen in a test tube to dry-ice temperature. The test tube is cracked off and the frozen mass dropped into 500 to 2500 cc of absolute alcohol. This mixture is shaken vigorously until the melting is complete. Vacuum filtration is started immediately, using a filter paper cut from typewriter bond. As soon as filtration is complete, the powder is vacuum desiccated. The size of crystals may be controlled slightly by varying the volume or temperature of the alcohol. Apparently no irregularity is introduced by over-chilling the alcohol with dry ice and letting it warm up until melting occurs.

(2) Crystals from 5 to 15 microns are precipitated by combining equal volumes of absolute alcohol and salt solution, with varying amounts of water up to 25 percent added to the saturated salt solution, as determined from Fig. 1B. Higher or lower temperatures give larger or smaller crystals. The solutions are handled in milk bottles, for heat insulation, and are poured together when they are exactly at the same temperature. The combined solutions are vigorously shaken for five minutes, vacuum filtered (using commercial filter paper), and vacuum desiccated immediately.

(3) For crystals from 10 to 70 microns, the same general procedure as for (2) is used, except that varying amounts of water, up to 3 percent, are added only to the absolute alcohol, in accordance with Fig. 1A. To prevent supersaturation from evaporation, 10 percent of water is added in all cases to the saturated salt solution. Temperature variations cause size variations as before.

Other methods tried and possible methods for extending the size range

Small particles were produced by pouring salt solution chilled to about 0°C into a filter already filled with absolute alcohol at dry-ice temperature. A sherbet was formed instantaneously as the salt solution entered the alcohol and was filtered as it melted.

Salt solution was sprayed from an atomizer under compressed air over a pan of absolute alcohol. The idea was that droplets of salt solution from the fine spray might precipitate individually to produce ultra-fine particles. It was difficult to keep irregular crystals from forming at the edges of the pan, and the process was tedious.

Various precipitants other than ethyl alcohol were tried: other alcohols, hydrochloric acid, ether, and combinations such as ether and alcohol. These gave interesting variations in several cases, but failed under preliminary examination to reveal possibilities beyond those of ethyl alcohol.

By deliberately working beyond the multiple range region of Fig. 1A, adding three to ten percent of water to the absolute alcohol, large crystals, mixed with distinct smaller crystals, were produced and separated by screening. No detailed study of the precipitation curves involved was made since large crystals were not needed for the present x-ray experiment.

Another method for accomplishing the same results as screening, and applicable to smaller ranges, was tried with considerable success. This was based upon Stokes' law for rate of fall of particles in suspension. Powder was placed in the lower end of a long glass tube, and a constant flow of absolute alcohol up through the column was maintained to separate all particles smaller than a certain size. The flow was then increased to obtain the next size, etc. The separation was better than from the usual precipitations but was very time-consuming, particularly for small crystals.

II. THE EFFECT OF CRYSTAL SIZE UPON X-RAY POWDER REFLECTION

Introduction²

Powdered crystals have been used in preference to single large crystals for many intensity meas-

urements on x-ray reflections. No assumption of perfect crystalline structure is necessary, and there remains only the assumption that the powder particles are so small that extinction is negligible in them. Havighurst¹ early showed that as powders were ground finer, reflection intensities increased to limiting values in agreement with theory; and indeed that, due to fracturing of crystals in grinding, the particles were effectively smaller than their physical dimensions. Subsequent standard practice has been to grind powders as fine as possible, and no effort has been made to study systematically the effects of using powders of crystals definitely larger than allowed by simple theory.

The simple method of preparing size-graded powders, presented in the first part of this paper, now makes possible such a study for sodium chloride without the complications of irregularities in ground crystals. In this direction, the intensity of the 200-reflection of Cu $K\alpha$ radiation has been measured as a function of particle size.

Apparatus

The x-ray reflection intensities were measured on the vacuum ionization spectrometer previously used by Allison and Jesse³ for determinations of structure factor decrements. The vacuum chamber, useful primarily to maintain the desiccation of the powders, is a part of the fore-vacuum line leading to the mercury pumps for the Dershem⁴ type x-ray tube. Both tube and mercury pumps are mounted on the removable cover of the vacuum chamber. The radiation is collimated to a 0.04×1.5 -cm beam by parallel steel plates and received after reflection by a 6.5-cm ionization chamber with fixed 0.15×1 cm slit. The ionization current is amplified by an external FP-54 Plotron circuit and read as deflections of a sensitive galvanometer. A screw turned through reduction gears by an electric motor moves the top of the spectrometer table, so that either of two powder briquets may be brought into the beam (without disturbing the vacuum) with a linear motion reproducible to 0.0001 in. The primary radius arm is 9 cm, from

² For a more complete introduction, the reader is referred to Chapter 6 of A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935).

³ S. K. Allison and W. P. Jesse, *Phys. Rev.* **49**, 483 (1936). W. P. Jesse, *Phys. Rev.* **52**, 443 (1937).

⁴ E. Dershem, *Rev. Sci. Inst.* **7**, 86 (1935).

central axis to either slit, but the long collimating slit prevents effective Bragg focusing.

For the present experiment, a copper target was installed, and the ionization chamber was filled with argon at 5 atmospheres. The $K\beta$ component was filtered out by a thickness of nickel sufficient to reduce the $K\alpha$ lines by 50 percent. In order that the FP-54 circuit might be operated at low amplification for stability, the power to the x-ray tube was increased to 14–28 ma d.c. at 35 kv, supplied by a full-wave kenetron 60-cycle rectifier circuit with $\frac{1}{3}$ mf filter condenser. The high potential, read from a large quartz-suspension electrostatic voltmeter, could be controlled to 0.2 percent. The filament current was supplied by storage batteries, and Dershem's⁴ positive grid arrangement was used at about 600 v d.c. The current through the x-ray tube, read from a galvanometer connected between ground and the floating filament system (including batteries and rectifier for the grid), could be controlled to 0.1 percent. A neon tube arrangement, in shunt across the galvanometer and series inductance, absorbed occasional pulses due to flash-overs in the x-ray tube, thus satisfactorily preventing null shifts of the galvanometer. Constant charging of the storage batteries supplying the Plotron circuit, at a rate equal to the drain, eliminated gradual changes of e.m.f. during long runs and also made it unnecessary to break into the sequence of runs for charging.

In the present experiment, one of the two briquets was changed before each run, introducing a source of error not encountered in previous experiments with this vacuum spectrometer. A variation of 0.001 in. in the linear position of successive briquet faces introduced an error of about 0.1 percent in the intensity reading, and it was necessary to construct a set of frames ($\frac{1}{8}$ in. thick), ground as nearly identical in thickness as possible.

Experimental procedure

All measurements were made by the "reflection method," according to the general plan used by Allison and Jesse.³ One powder was selected as an arbitrary standard against which all others were to be compared, and this briquet was mounted permanently throughout the experiment as one of the two powders on the spectrometer table. Thus no absolute measurements of intensity were made. A run consisted of recording four or more successive intensity curves, taken alternately for the standard and the powder under test. Each curve consisted of a set of about thirty points—always the same set—so chosen as to show the maximum detail of the intensity curve. These points, separated by crystal angle increments of from 1 to 10' and covering a total angle interval of 3° 50', extended about 45' to either side of the main broad rise of the intensity curve. The last three points on either side were assumed always to represent the

TABLE I. Observed reflection intensity as a function of particle size.

No. (Fig. 3)	DATE	CRYSTAL SIZE			RELATIVE INTENSITY	PERCENT OF DEVIATION	REMARKS
		MIN.	AV.	MAX.			
1	4-6	3.4	5.6	6.7	1.040	1.1	Preliminary test run
2	4-7	(No. 1, repeated)			1.053	1.1	
3	4-8	31	40.6	43	0.745	0.2	
4	4-9	0.6	1.15	2.3	1.098	0.7	Rinse used for binding Irregular crystals
5	4-10	0.7	3.0	3.4	1.127	0.2	
6	4-11	0.6	1.25	2.5	1.179	1.3	
7	4-14	5.6	8.80	10.7	0.910	0.4	Transformer burned out
8	4-15	9.6	14.8	17.3	0.820	0.3	
9	4-17	16.0	20.0	20.6	0.870	—	
10	4-19	1.7	3.55	3.8	1.116	0.9	Imperfections within crystal cubes
11	4-20	(No. 5, repeated)			1.121*	0.5	
12	4-22	(No. 5, repeated)			1.135*	0.6	
13	4-27	(No. 6, repeated)			1.173*	0.2	Redesiccated crystals
14	4-28	3.7	6.0	7.0	1.160*	0.0	
15	4-29	0.9	1.47	1.7	1.146*	0.4	
16	4-30	0.7	1.65	3.1	1.133*	0.8	Slightly irregular crystals
17	5-2	0.7	1.5	2.4	1.148*	0.4	
18	5-3	(No. 7, repeated)			0.951*	0.5	

* Values have been increased by a correction factor of 2.23 percent.

background base line, thus reducing any error from base line choice. The area under each intensity curve above the base line was determined, and the ratio of the areas for the two powders under test was computed as the final numerical result of each run, by averaging the two ratios, $B/\frac{1}{2}(A+C)$ and $\frac{1}{2}(B+D)/C$,⁵ where A , B , C , and D are the four areas. Areas were obtained by adding ordinates times half the abscissa increments on either side of each point.

The four coarsest powders tested contained crystals of sizes no longer negligible as compared to the slit widths, causing the intensity curves to be irregular. In these instances, an extra run was made with as many additional points as necessary to resolve the entire detail. Two areas were computed—one from the usual set of thirty points abstracted from the larger number, the other from all the points. The ratio of these was considered to be an accurate correction factor by which the areas from the other runs were to be multiplied. The largest value of this correction was 1.4 percent.

The spread of ratios for any one run was usually less than 1 percent, and the average was considered precise to 0.5 percent. This was borne out by repeating runs on successive days without changing the powder under test. However, discrepancies of the order of 1.5 percent occurred when briquets once removed from the spectrometer table were replaced and tested again. These shifts were found to be due to some play in the supports of the steel plates against which the briquets were mounted. Only a major redesign of this portion of the apparatus would have eliminated this greatest source of error. In view of the irregularities which variations from the crystals themselves were found to produce, this seemed unnecessary.

Experimental results

Table I and Fig. 3 present the final experimental results. The determinations were made in random order to avoid systematic error from gradual changes in the apparatus. The values in the table marked with an asterisk have been obtained by multiplying the original values by

⁵ The "Percent of Deviation" column of Table I represents the difference between these two ratios.

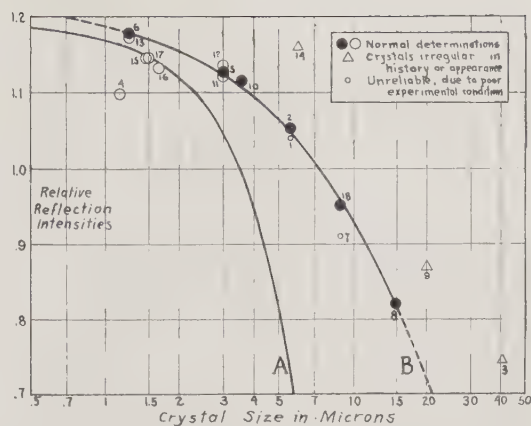


FIG. 3. Experimental observations and related theoretical curves. Curve B has been adjusted to fit the dark-centered points.

the correction factor, 1.0223, to account for a shift in the alignment of the apparatus when the set screw on one of the briquet supports was jarred. This was obtained by comparing values for 11, 12, and 13 with those for 3 and 6. Large circles, dark or open centers, are used in the figure for determinations involving no irregularities in the crystals or in the behavior of the x-ray equipment.

The three determinations indicated in Fig. 3 by triangles involve powders of such definite irregularity in history or appearance that their wide deviation from the general curve might almost be anticipated. The powder for No. 14 had undergone a previous desiccation and had been shaken again in absolute alcohol, packed into the briquet frame, and redessicated. Although there was no mechanical action involved which would have been expected to produce fracturing or scratching, the crystal structure seems to have been changed. The powders of No. 9 and No. 3, corresponding to the 20μ and 40.6μ crystals of Fig. 2, contained many internal imperfections; and No. 3, too coarse to adhere in the briquet frame under the usual conditions, had to be treated with salt-saturated 80 percent alcohol before desiccation. Internal imperfection is evident to a smaller degree for all the larger crystals, but is almost absent in small crystals, as can be seen for the 5.6μ and 3μ crystals of Fig. 2. The intensity of reflection is abnormally high for each of the three points represented by triangles, as might be expected from decrease of

extinction effects with increase of imperfection in the crystalline structure.

There is little doubt that the intensity values are accurate to 1 or 2 percent. It must be stressed, however, that the crystal sizes cannot be fixed with comparable accuracy. This is caused, first, by the range of crystal size within a powder, making the average size dependent upon the type of average. The type of average attempted here was based on total *volume* of crystals within each size increment; an average based on *number* would be considerably lower.⁶ Since no distribution measurements were attempted, it is unlikely that the averages shown express exactly the ideal. An error of this type might shift the curve to the right or left by a factor of as much as 15 percent. But secondly, the extreme limit of resolution of the microscope did not allow measurement of a dimension difference less than 0.3μ . Thus the six points in the 1 to 2μ range may be in error by as much as 40 percent. However, it is likely that the sizes are in the order shown,⁷ and a more accurate determination of sizes would probably not bring these points into a smooth curve. It might be mentioned that oil immersion decreased rather than increased the resolution of detail because of the high index of refraction of rocksalt. Several powders of crystals larger than those for which points are shown were prepared, but intensity curves from runs on these were too irregular to be considered valid.

Theory

A detailed comparison of the experimental results with theory will not be attempted here, but certain obvious conclusions can be pointed out. The relative intensities observed are proportional to values which, due to extinction, are less than the standard theoretical reflection power from a briquet of ultra-fine crystals:⁸

$$P = P_0 \frac{j l}{16 r \sin \theta} \frac{\rho'}{\mu_p \rho} \quad (1)$$

⁶ The averages shown in Table I, thus stressing volume, are slightly higher than those of Fig. 1, and "maximum" and "minimum" are slightly more inclusive than the previous "normal maximum" and "normal minimum."

⁷ Re-measurements on No. 4 indicate that this powder varies in size at different parts of the sample.

⁸ Derived in full in A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, 1935), Eq. (6.85), p. 419.

P is the power intercepted by a broad slit of length l at a distance r from the powder; P_0 is the incident power; j is the permutation constant, 6 for the 200-reflection of NaCl; θ is the Bragg angle of reflection; μ_p is the effective linear absorption coefficient of the powder, and ρ' and ρ are, respectively, the density of the powder and the density of the crystalline material in unpowdered solid form.

Since $\mu_p = \rho' \mu_m$, where μ_m is the mass absorption coefficient of NaCl, and since μ_m and ρ are constant, Eq. (1) reduces to

$$P = k P_0, \quad (2)$$

where k is a constant of the apparatus and the reflection, independent of density of packing.

There are two assumptions involved in obtaining Eq. (1) which may not be fulfilled in the present experiment. First, it is assumed that there is negligible decrease in irradiation intensity within those few individual crystals aligned for Bragg reflection, whether due to normal absorption or to extinction. The present crystals were so large as to violate this assumption, definitely resulting in shielding of the deeper reflection planes by the upper planes, with consequent decrease of total power of reflection. The second assumption is that the decrease of irradiation intensity through the powder as a whole, because of normal absorption in individual crystals, is sufficiently continuous for integration according to a simple absorption curve based on a constant μ_p . Since even large irregularities probably tend to average out, it would seem that this assumption is much less critical than the first. It should be mentioned, however, that normal linear absorption in the largest crystals used was of the order of 40 percent.

Returning to the first assumption, if the particles could be considered perfect crystals, full primary extinction would occur and result in large shielding effects. While there is no theoretical equation available exactly expressing the average effects from uniform cubes, some idea of the variation to be expected can be obtained from Waller's⁹ expression for the ratio R_A of the power as reduced by primary extinction to the power given by Eq. (2), in the case of

⁹ I. Waller, *Ann. d. Physik* **79**, 261 (1926).

crystal slabs of thickness t :

$$R_A = \frac{1}{\pi A} \int_0^{\pi/2} \frac{\sin(2A \sin \varphi)}{\sin \varphi} d\varphi, \quad (3)$$

where

$$A = \frac{e^2 \lambda}{mc^2} \frac{F}{V} \frac{t}{\sin \theta}.$$

e , m , c , and λ have the usual significance; F and V are the structure factor and the volume, respectively, of the unit NaCl crystal cell; θ is the Bragg reflection angle.

This equation has been plotted as curve A of Fig. 3, from unpublished simplifications by W. A. Zachariasen, with t considered equivalent to the linear dimension of the cubes as an approximation. From comparison of this curve with the experimental points, one logically concludes that the crystals are somewhat imperfect, as though constructed of smaller perfect crystals. This would be expected from the internal imperfections evident in Fig. 2, although no direct correlation as to the exact size of these inner crystals should be attempted. The points for intensities observed for small crystals, characteristically more perfect than large crystals (Fig. 2), lie very close to curve A .

Since Bragg, James, and Bosanquet¹⁰ obtained consistent results for transmission through varying thicknesses of large single crystals by considering secondary extinction as a constant addition to the ordinary absorption coefficient, it was thought that such a treatment might be applicable to the present case. Computations were made (without approximation) of R_B , the ratio of the intensity reflected from Bragg-aligned cubes, averaged over various possible angular positions (about an axis perpendicular to reflecting planes), to the intensity that would be reflected if no absorption were taken into account. Curve B of Fig. 3, showing the best fit to the dark-centered points, which represent a series of powders thought to be similar in preparation and appearance, corresponds to an absorption coefficient thus computed to be in excess of the normal absorption coefficient (130)

by about 300. That this is considerably higher than the approximately 50 percent excess found by Bragg, James, and Bosanquet¹⁰ for large single crystals suggests that the present small crystals are more perfect than most large crystals. A more precise significance than this should not be attached to the numerical value 300, since the extinction excess to the absorption coefficient cannot be treated as a constant for perfect crystals or for crystals in which the mosaic blocks are large. It should be noted that the appearance of close agreement between curve B of Fig. 3 and the experimental points has little significance, since the curve was adjusted (in both coordinates) to fit the points. On the other hand, the abscissas of curve A are fixed at absolute values; and the ordinates, although adjusted, permit of little variation.

Thus from this incomplete theoretical analysis of the x-ray data, it appears that the crystals are imperfect but are more perfect than large crystal specimens.

Conclusion

Powders of well-formed, uniform sodium chloride crystals in a variety of sizes may easily be produced by the method described in the first part. The intensity of x-ray reflection from these powders indicates that the crystals, although imperfect, are composed of mosaic blocks which are larger or better aligned than is usual for large single crystal specimens. These intensities are affected by the method of preparing the crystal powders.

It would be of great interest to develop a similar method for producing uniform size-graded crystals of calcite, which has been found almost unique in its tendency to form perfect large crystals. It might very well be expected that reflection intensities would correspond to full primary extinction effects.

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¹⁰ Bragg, James and Bosanquet, Phil. Mag. **41**, 309 and **42**, 1 (1921).

